IDECAT WP3 Seminar

Prag

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High pressure XPS: A tool for the investigation of heterogeneous catalytic processes

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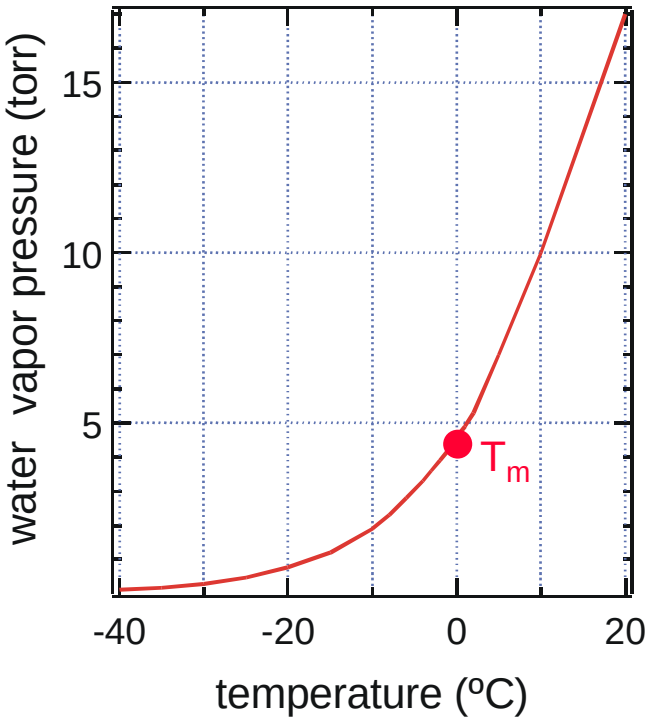
Why in situ XPS ?

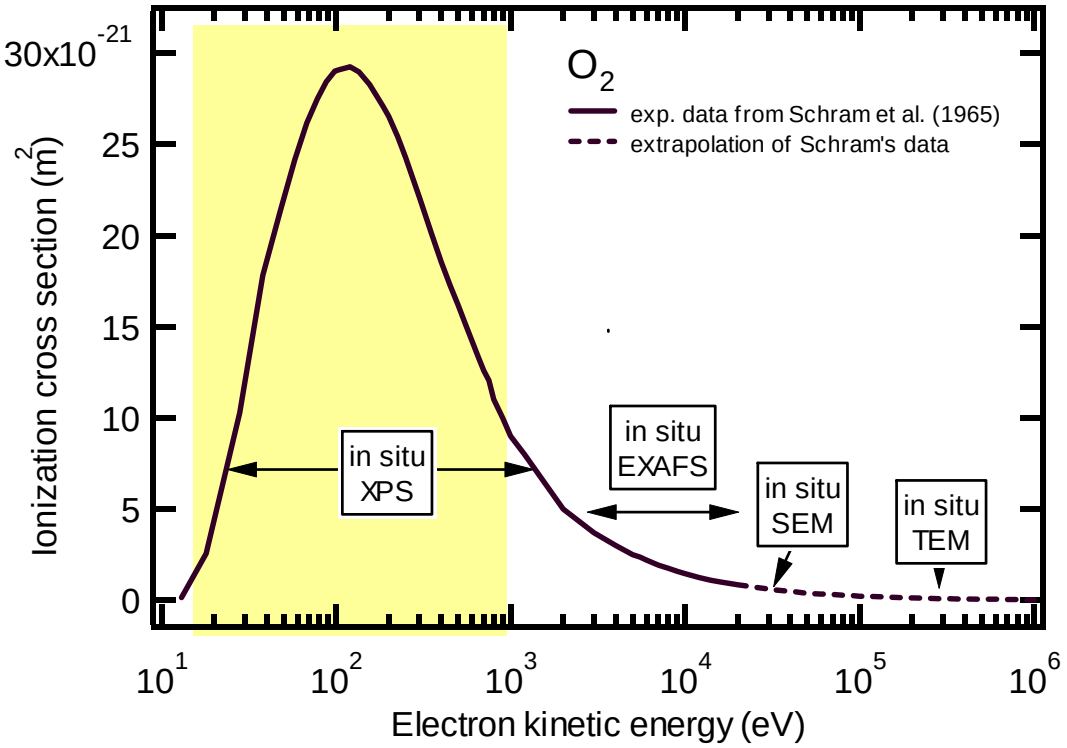
- Many processes cannot be investigated in UHV: "Pressure Gap"
  - **environmental chemistry**
  - **catalysis**
  - corrosion
  - electrochemistry
  - biological samples
- Very few methods can investigate the solid-gas interface at high pressures
  - non-linerar optics (SFG, SHG)
  - scanning probe microscopies
  - X-ray diffraction
- Photoelectron spectroscopy is very powerful
  ⇒ Goal: XPS at pressures of at least 5 torr



In situ XPS: obstacles

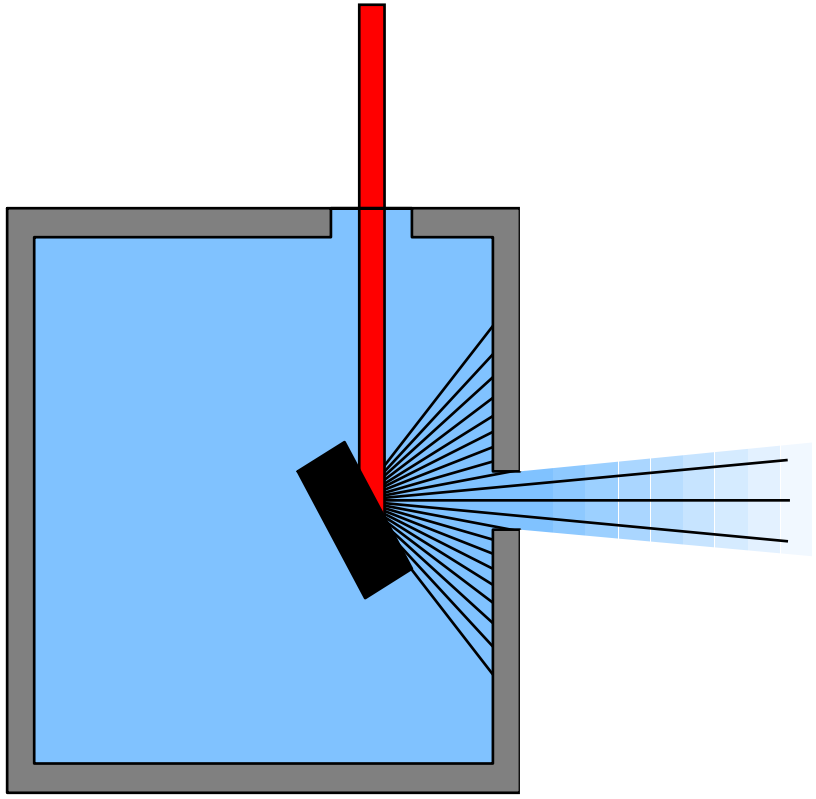
Fundamental limit:

elastic and inelastic scattering of electrons in the gas phase



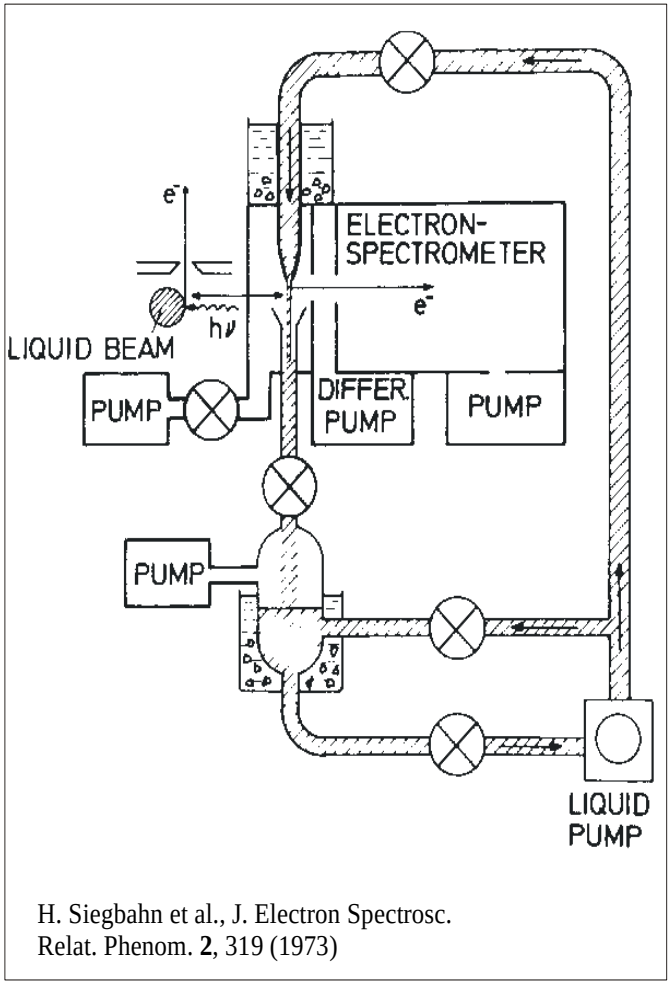
Technical issues:
- Differential pumping to keep analyzer in high vacuum
- Sample preparation and control in a flow reactor

In situ XPS: basic concept



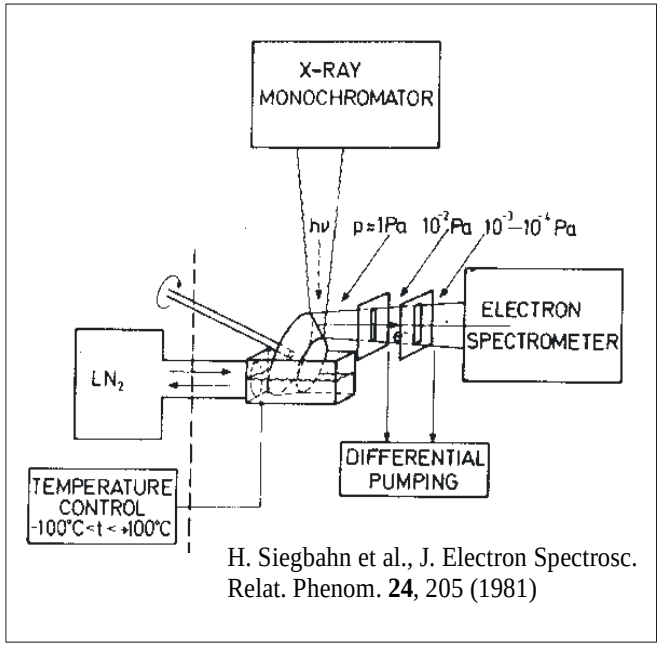
- Photons enter through a window
- Electrons and a gas jet escape through an aperture to vacuum

In situ XPS instruments: previous designs



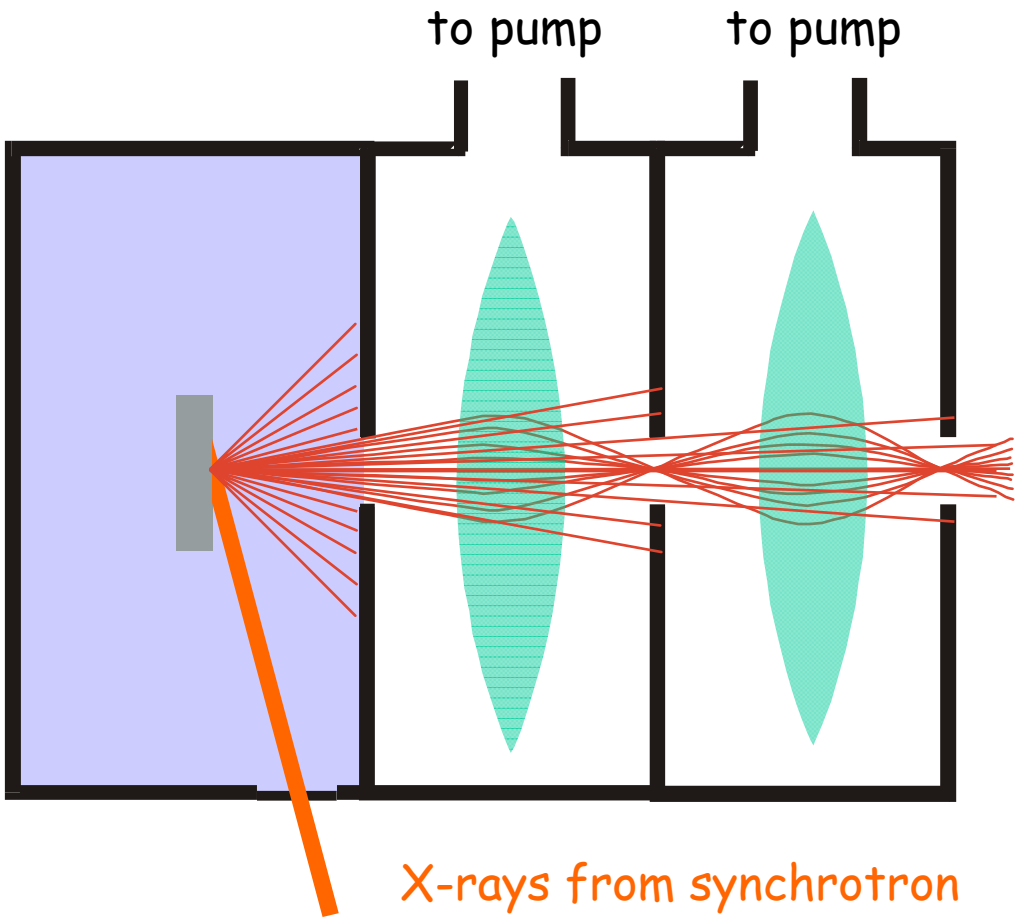
H. Siegbahn et al., J. Electron Spectrosc. Relat. Phenom. **2**, 319 (1973)

- H. Siegbahn et al. (1973-)
- M.W. Roberts et al. (1979)
- M. Faubel et al. (1987)
- M. Grunze et al. (1988)
- P. Oelhafen (1995)



H. Siegbahn et al., J. Electron Spectrosc. Relat. Phenom. **24**, 205 (1981)

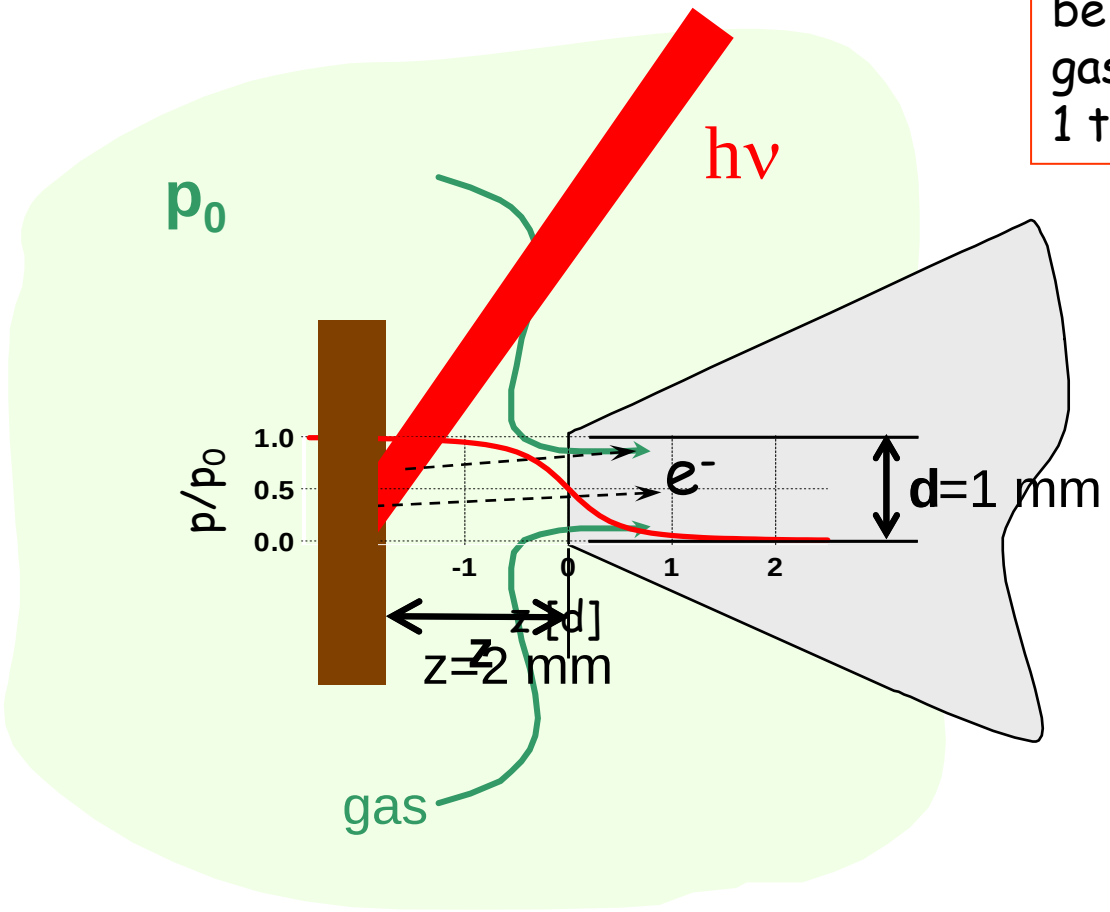
In situ XPS using differentially pumped electrostatic lenses



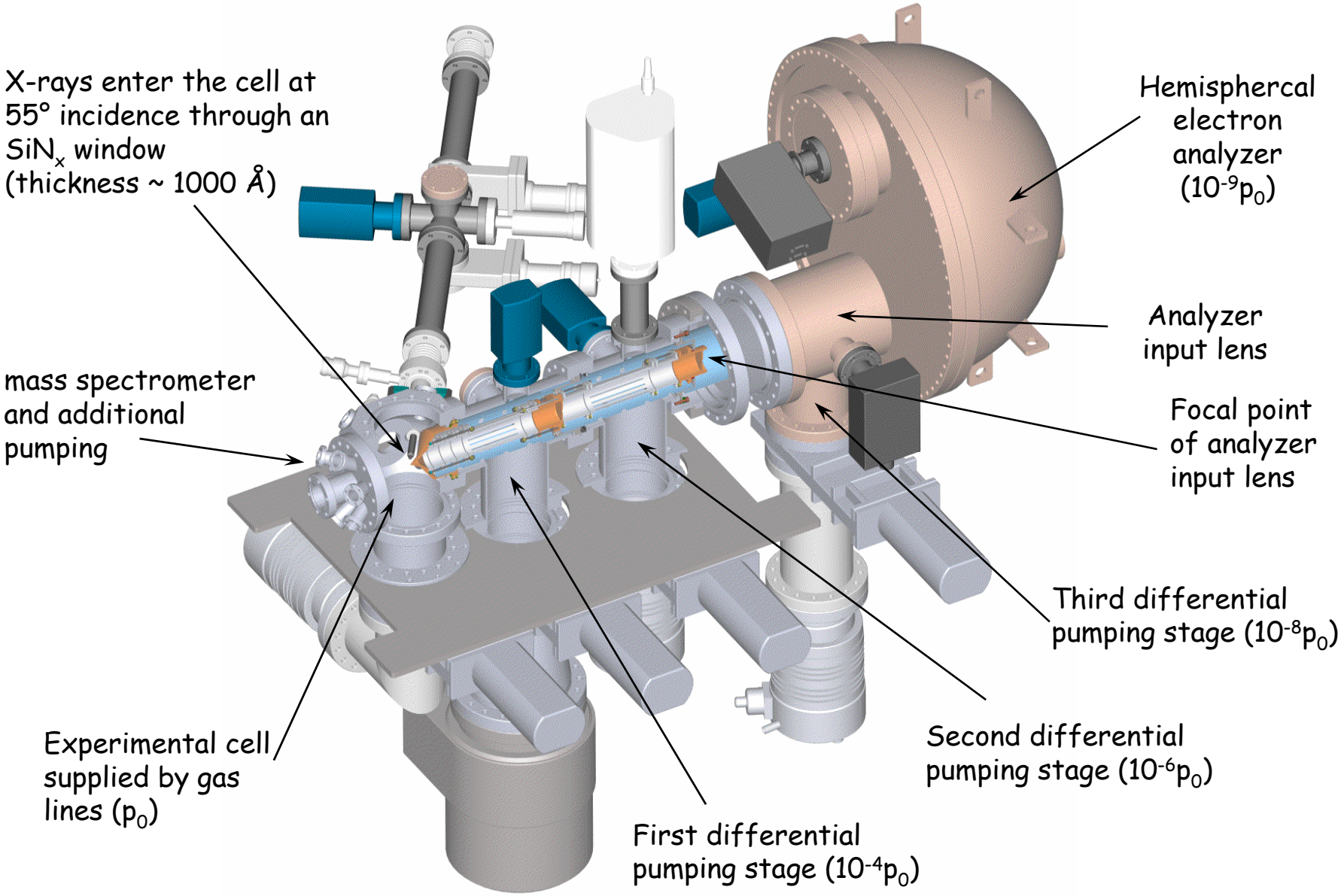
D.F. Ogletree, H. Bluhm, G. Lebedev, C.S. Fadley, Z. Hussain, M. Salmeron, Rev. Sci. Instrum. 73 (2002) 3872.

Close-up of sample-first aperture region

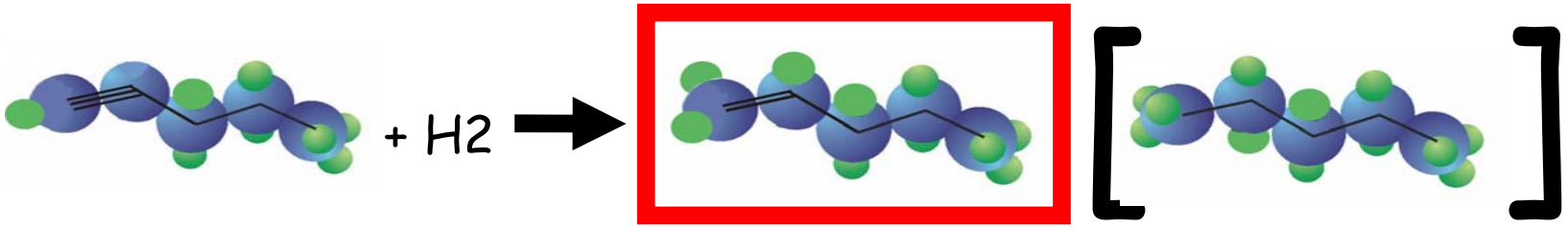
Gas phase composition can be measured by XPS.
gas phase signal:
1 torr·mm ~ a few monolayers



In situ XPS system



Introduction



Literature

carbon laydown → selective hydrogenation

"similar" catalysts → different activity & selectivity

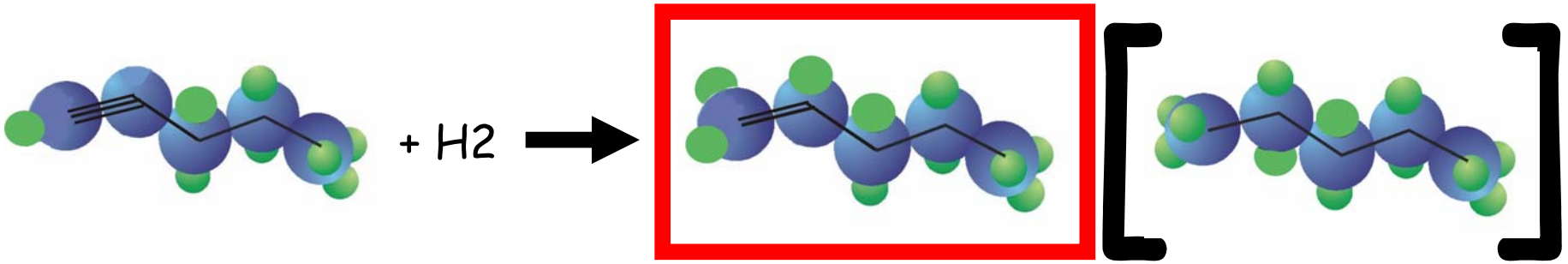
(structure sensitivity?)

Selectivity issue: what defines selectivity?

Summary

1. *Subsurface H*: effective for alkene-to-alkane but also for alkyne-to-alkane transformation
2. *Surface H*: could be selective (spillover)
3. *Different reaction orders* in the different selectivity regimes & Abrupt changes between regimes
4. *C uptake* is significantly more in the selective regime

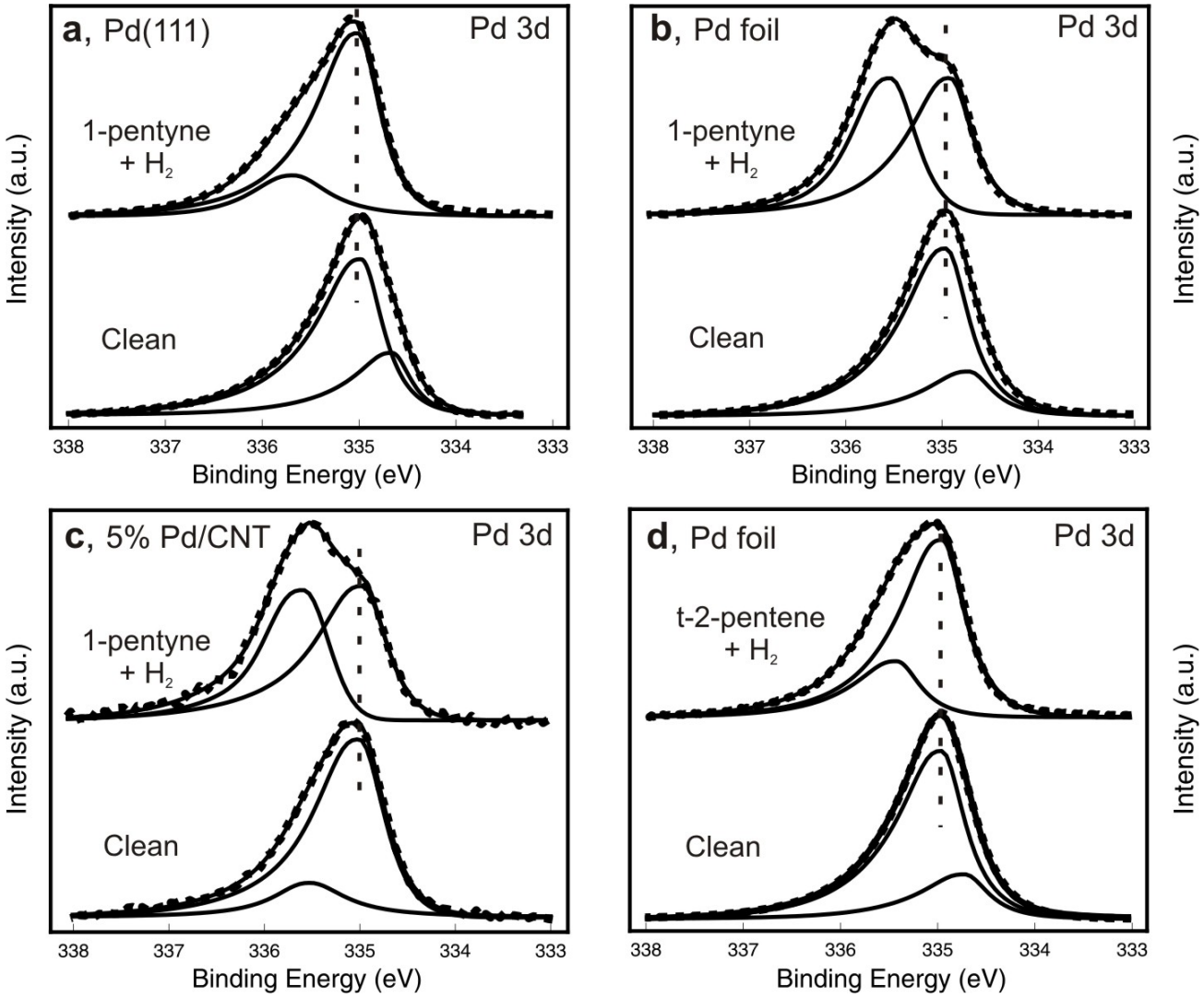
Reaction in the mbar p region (in-situ XPS)



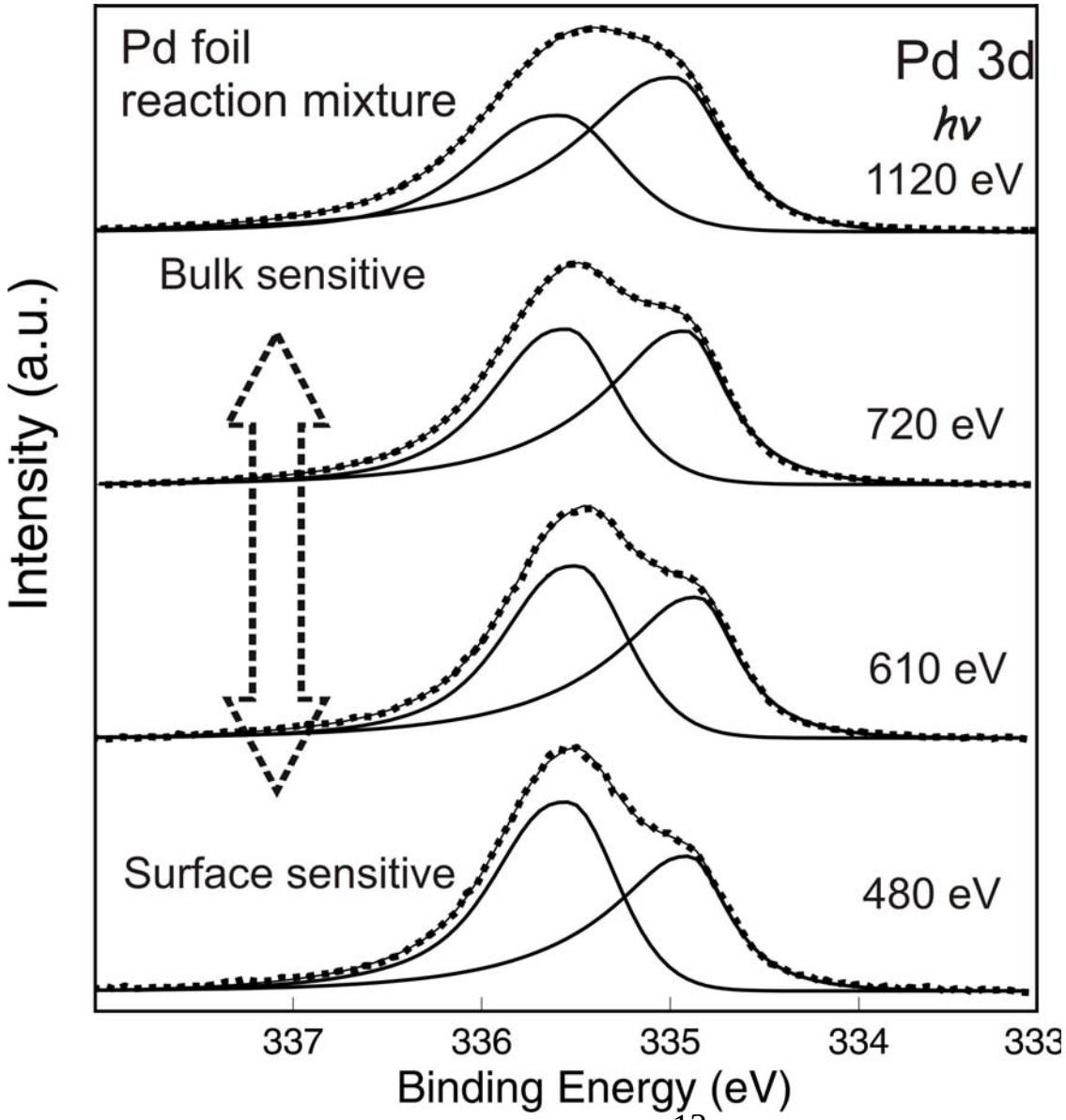
	5% Pd/CNT	3% Pd/Al_2O_3	Pd foil	Pd(111)
Conversion [%]	~ 10	~5	~2.5	<1
Selectivity Pentene [%]	~95	~80	~98	100
Selectivity Pentane [%]	~5	~20	~2	-

Recation conditions: C5/H2 = 1:9, 1 mbar, 358 K

In-situ XPS: Pd 3d (hν: 720 eV)



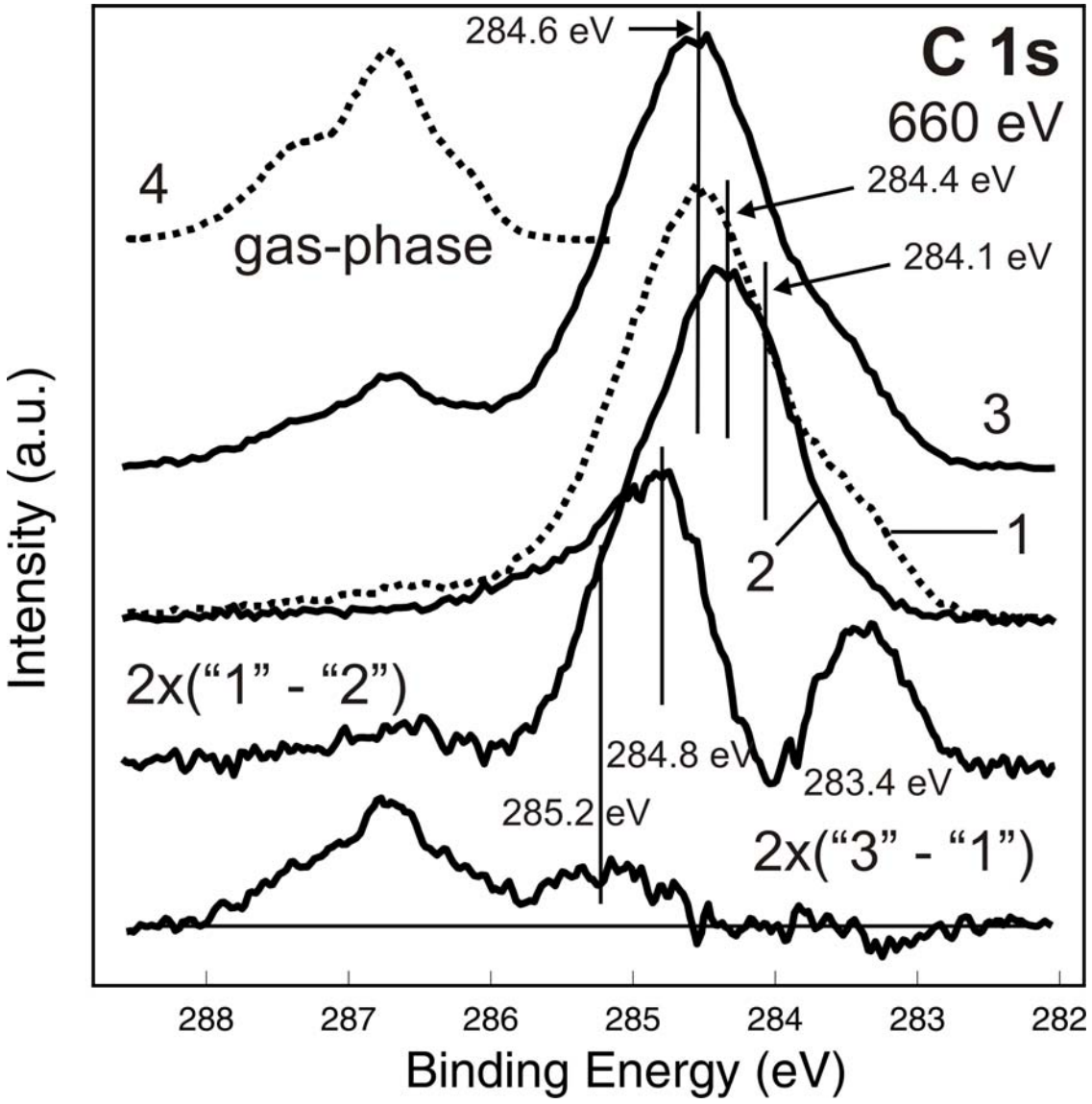
In-situ XPS: Pd 3d depth profiling



Not only adsorbate-induced surface core level shift !

But on-top location!

In-situ XPS: C1s (Switching off experiments)



1: reaction mix.

2: C5 off

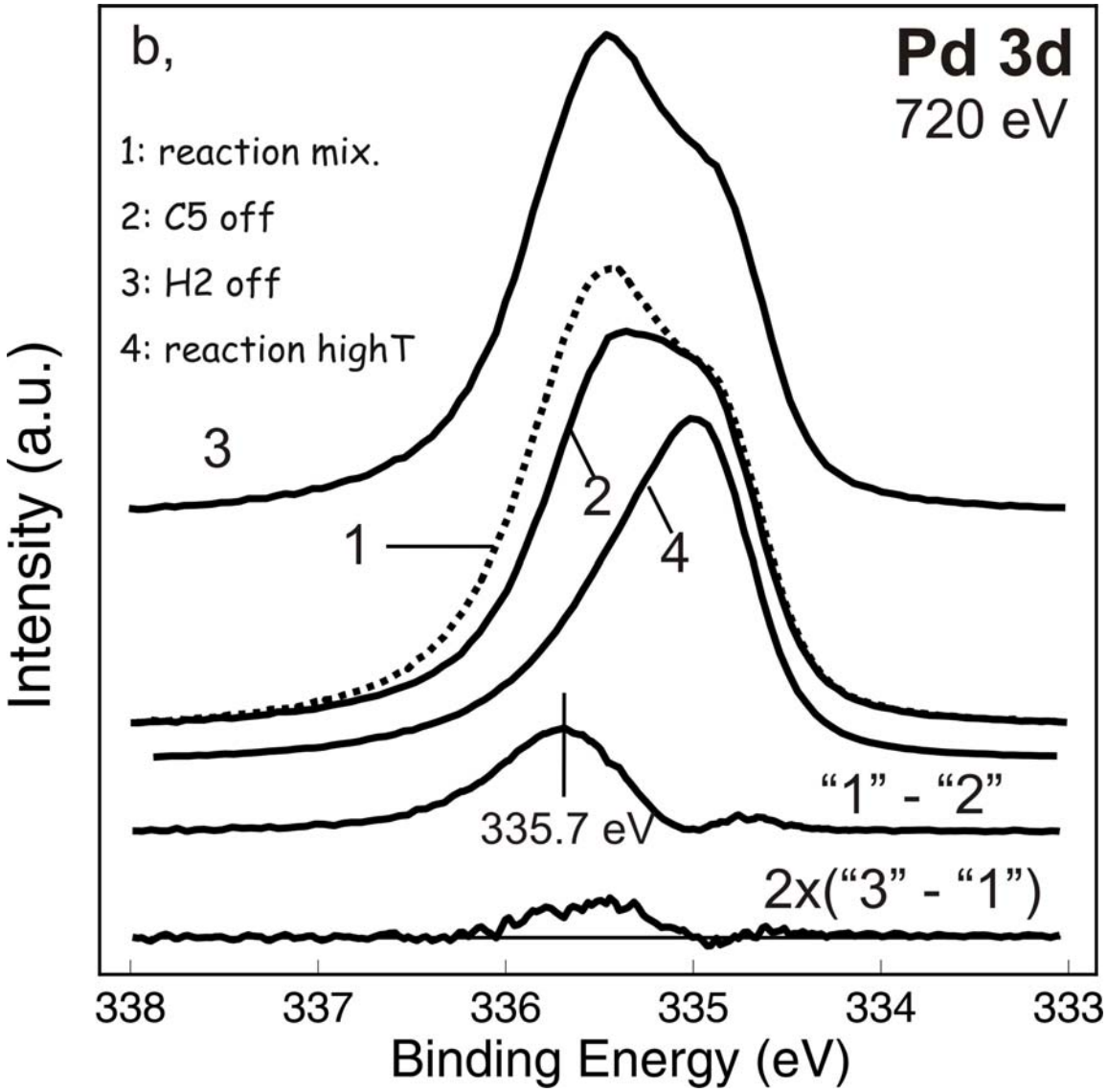
3: H2 off

4: C5 gas-phase

Teschner et al.

J. Catal. 242 (2006) 26-37

In-situ XPS: Pd 3d (Switching off experiments)



1: reaction mix.

2: C5 off

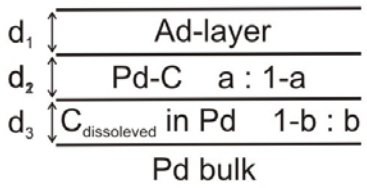
3: H2 off

4: reaction; high T

523 K

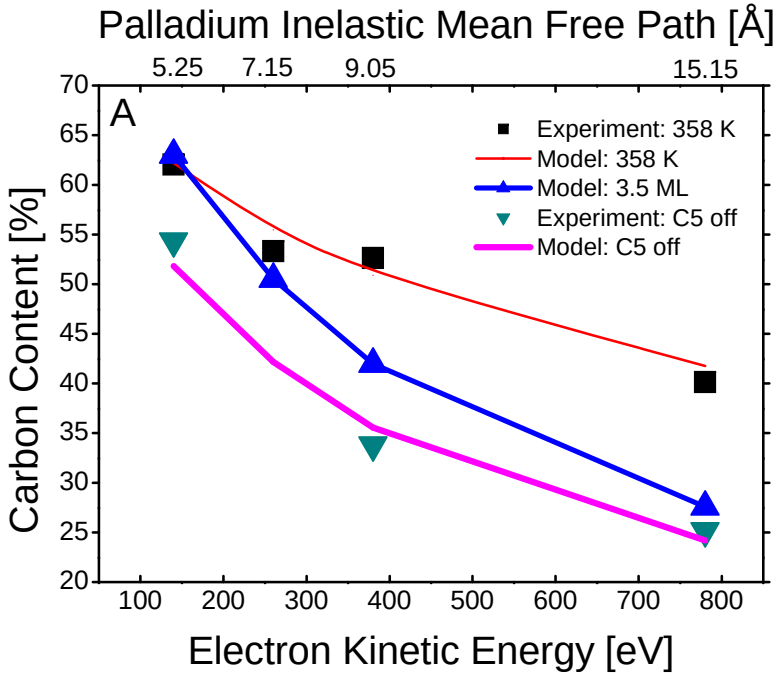
In-situ XPS: Pd vs. C depth profiling

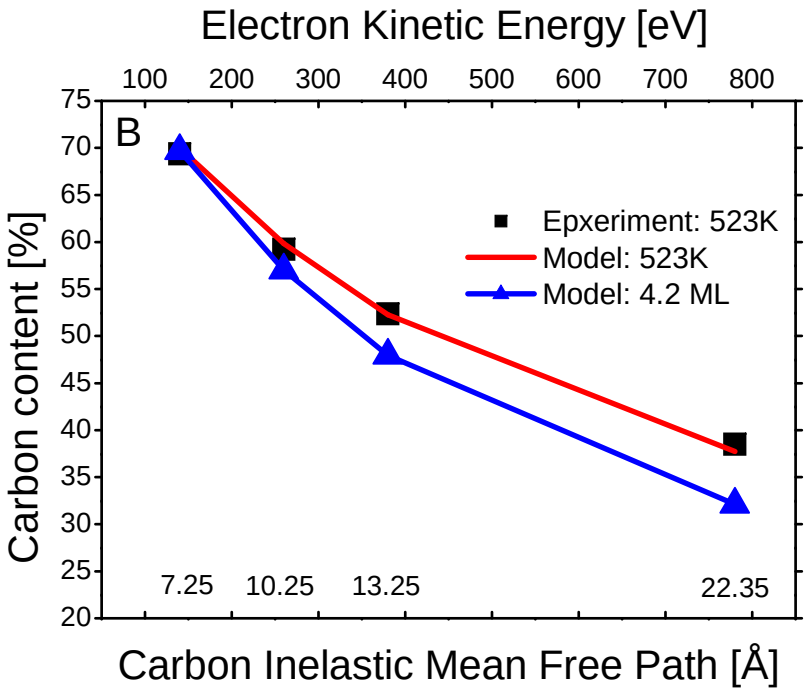
Model



=

0.3 nm
1.4 nm
14 nm





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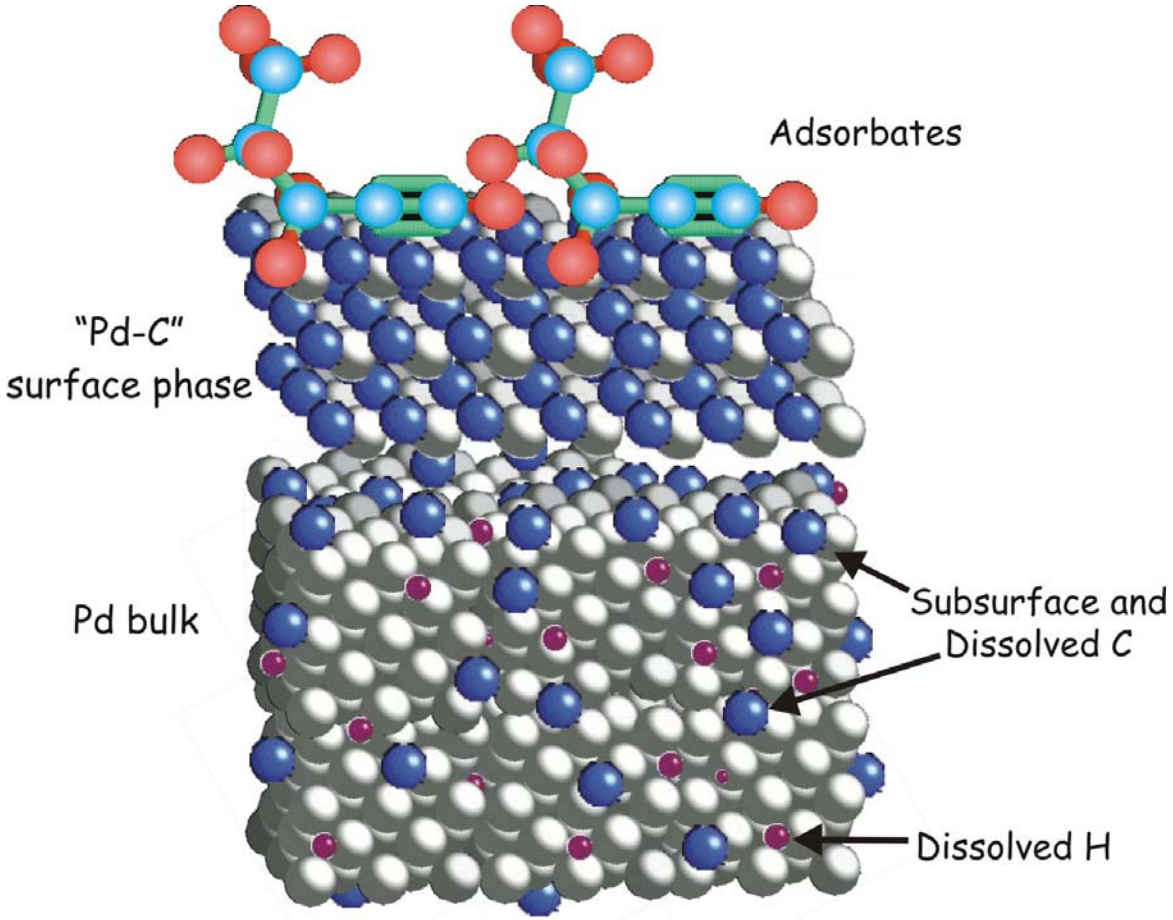
5. *Pd-C surface phase* forms in the early stage of selective pentyne hydrogenation & there is significant amount of *subsurface C* below of it

Model (during the reaction)



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5. *Pd-C surface phase* forms during selective hydrogenation of pentyne & there is significant amount of *subsurface C* below of it
6. Dynamic behaviour of Pd-C and subsurface C

Outlook: In situ XPS / XAS
The future at BESSY

BESSY ISISS:

Innovative Station for In Situ Spectroscopy

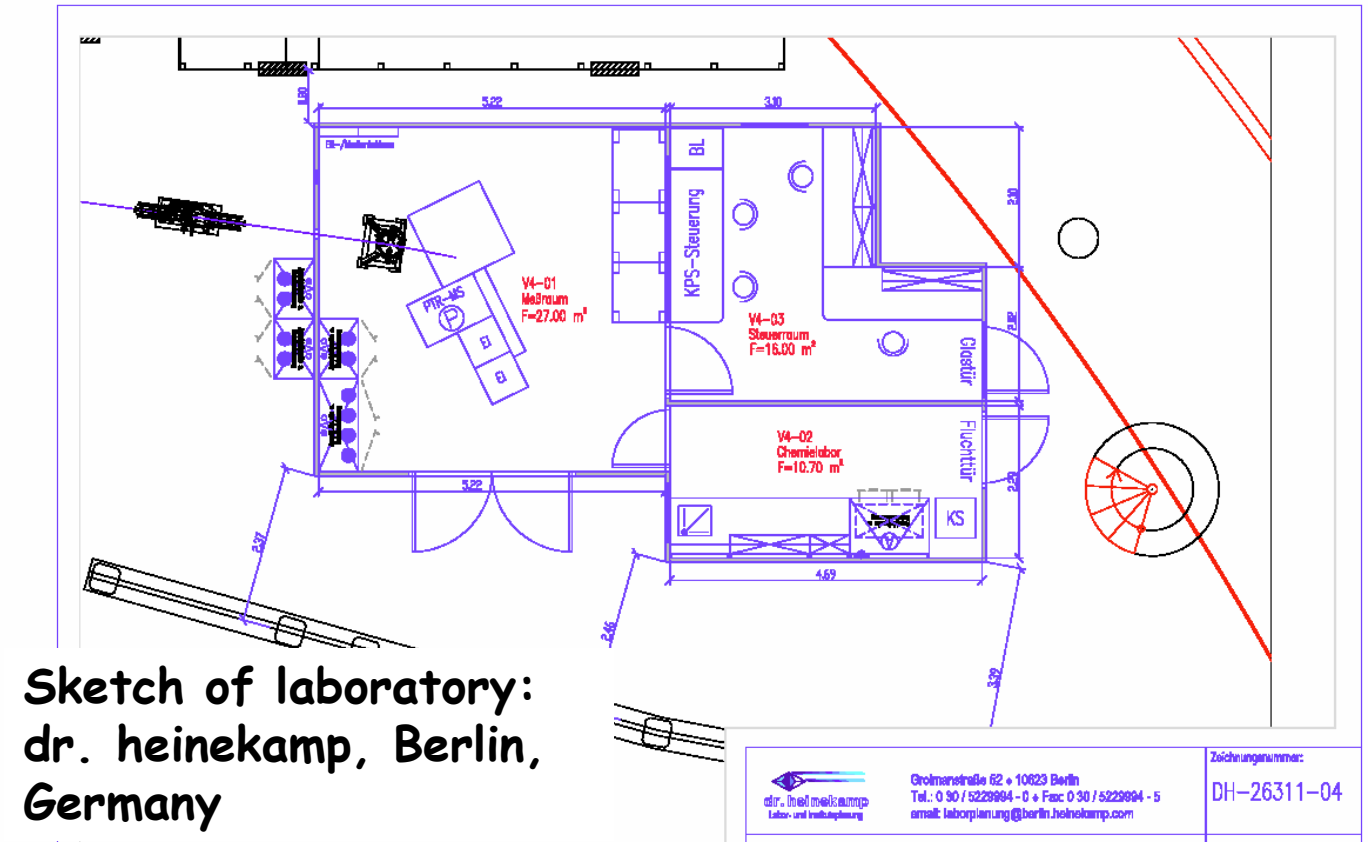
A project of BESSY and the Dep. Inorganic Chemistry, Fritz-Haber-Institut

- Installation of a beamline exclusively used for in situ spectroscopy in the soft X-ray range
- Installation of infrastructure optimized for these kind of experiments on site (e.g. chemical lab, gas supply, gas analytics)
- Later, further implementation of other in situ spectroscopy techniques: multi wavelength Raman, UV-Vis, fluorescence yield ?!
- Start of user operation of the beamline: 2007

Outlook: In situ XPS / XAS
The future at BESSY

BESSY

ISISS:



Sketch of laboratory:
dr. heinekamp, Berlin, Germany

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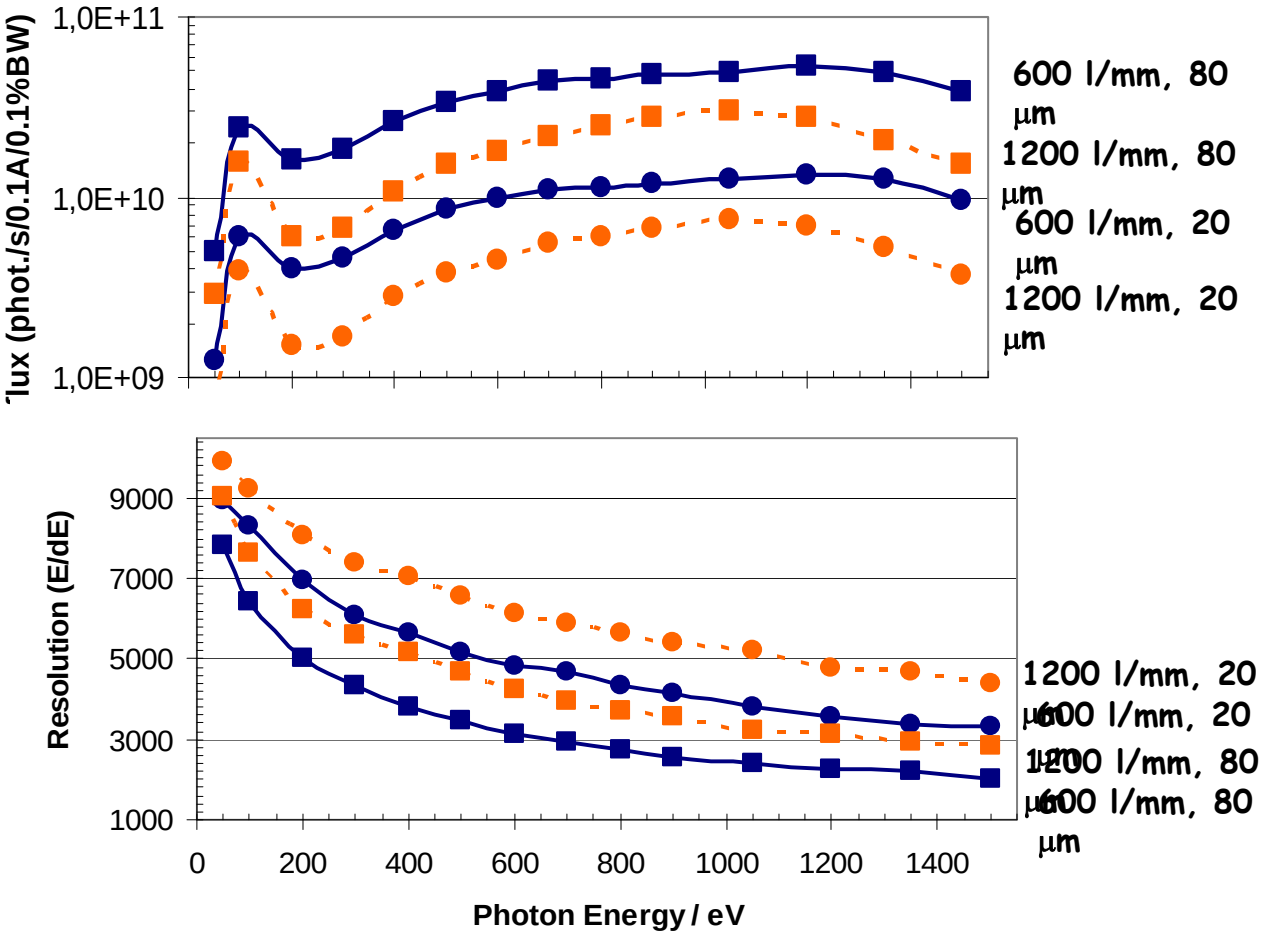
The future at BESSY



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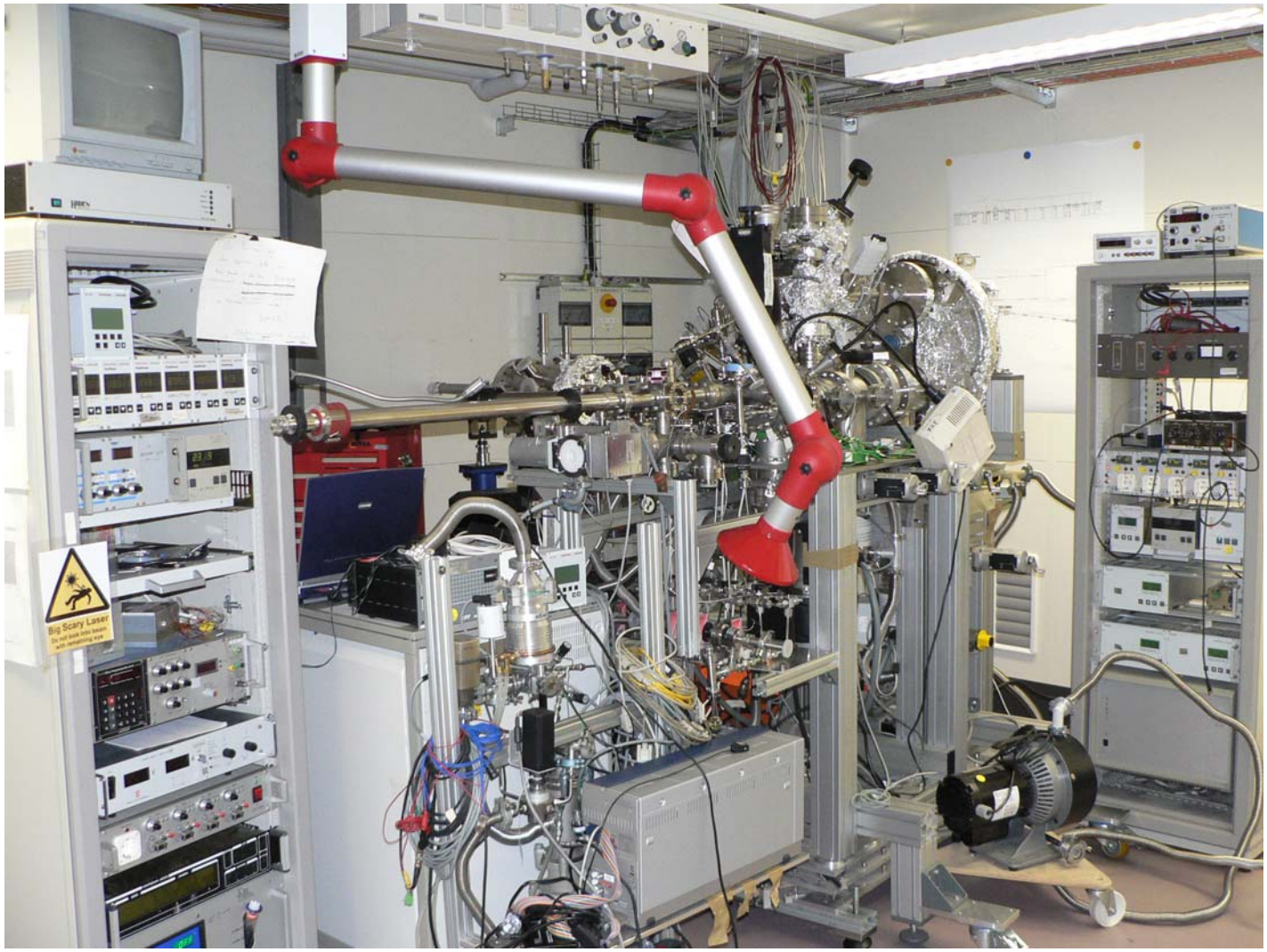

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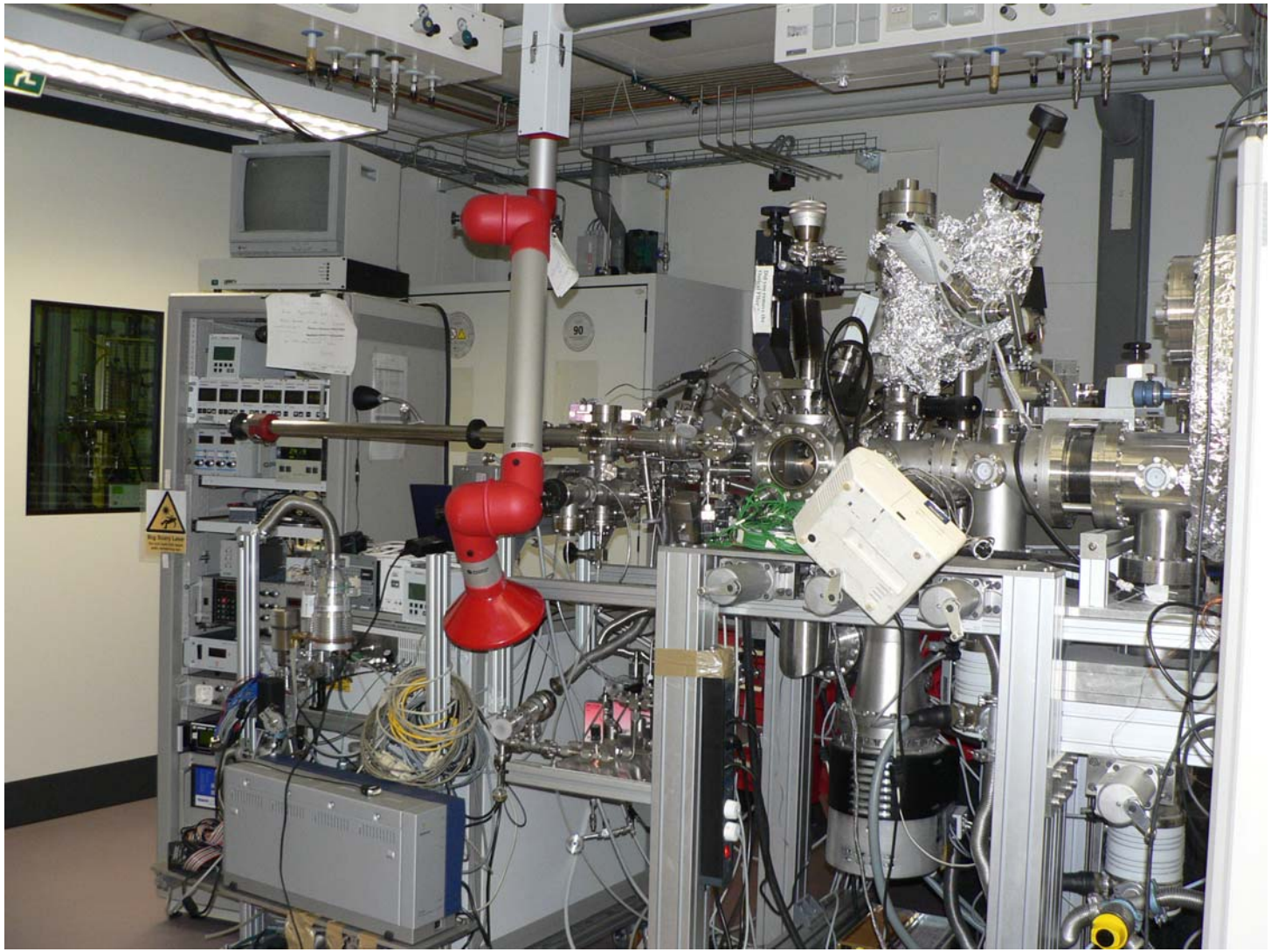

Outlook: In situ XPS / XAS
The future at BESSY

Thanks to:

- Detre Teschner, Elaine Vass, Michael Hävecker, Evgueni Kleimenov,,Spiros Zafeiratos, Péter Schnörch, Hermann Sauer, Robert Schlögl (FHI, Dept. AC)
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